

# Magnetism in purple bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$

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## Abstract

Muon spin relaxation measurements around the 25 K metal-insulator transition in  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  elucidate a profound role of disorder as a possible mechanism for this transition. The relaxation rate  $1/T_1$  and the muon Knight shift are incompatible with the transition to a SDW state and thus exclude it.

## Key words:

Low-dimensional magnetism; impurity in Tomonaga-Luttinger liquid; Kondo impurity; muon spin resonance.

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Recent optical studies of the ternary molybdenum oxide bronzes  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  have kindled new interest in the electronic properties of inorganic quasi-1d transition metal compounds.[1]  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  (a purple bronze) exhibits a particularly interesting set of electronic and magnetic properties. For instance, in a recent series of ARPES measurements it has been suggested that the ground state for this system is the Tomonaga-Luttinger liquid.[2]  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  has a monoclinic crystal structure [ $P121/m1(11)$ ] and a unit cell consisting of four  $\text{MoO}_6$  octahedra and two  $\text{MoO}_4$  tetrahedra (see Fig. 1). The crystal structure is formed by stacking layers ( $a - b$  planes) of corner sharing octahedra and tetrahedra.  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  has a highly anisotropic metallic conductivity down to 25 K, where its resistivity exhibits an upturn and resembles that of a semiconductor. At 2 K the material undergoes a transition to a BCS superconducting state. Despite extensive (and ongoing) studies of the transition at 25 K, its nature is still rather puzzling. The following models have been proposed as likely candidates: CDW, SDW and localization driven by disorder.[3]

Muon spin relaxation ( $\mu\text{SR}$ ) is sensitive to magnetic transitions in a large variety of systems, so we performed high transverse field (hTF) and zero field (ZF)  $\mu\text{SR}$  experiments on  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  with particular attention to the 25 K transition, to clarify its magnetic nature.

All the measurements were performed on the M15 beamline at TRIUMF, which delivers nearly 100% spin polarized positive muons with a mean momentum of 28 MeV/c. The muon spin polarization was rotated perpendicular to the axis of the superconducting solenoid and muon beam direction. The magnitude of the applied magnetic field,  $H = 55$  kOe, was chosen to provide a balance between the magnitude of the frequency shift, which increases with field, and the amplitude of the  $\mu\text{SR}$  signal, which eventually diminishes with increasing field due to the finite time resolution of the detectors. The transverse field precession measurements were all performed with a special cryostat insert which allows high-field  $\mu\text{SR}$  spectra to be acquired in the sample and in a reference material ( $\text{CaCO}_3$ ) simultaneously.

Muon Knight shift data were taken on a powder sample of  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ . The magnitude of the shift was calculated as  $K = (\omega_\mu - \omega_L)/\omega_L$ , where  $\omega_\mu$  is the  $\mu^+$  precession frequency in the sample and  $\omega_L$  is that in

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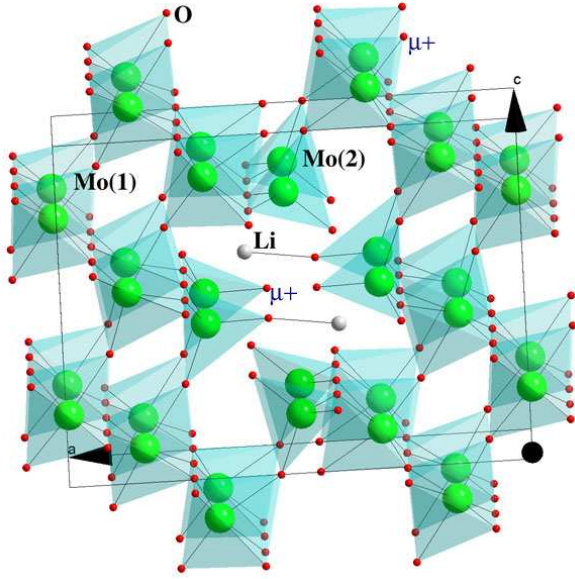


Fig. 1. A purple bronze unit cell. The molybdenum ions are located in an octahedral and a tetrahedral environment, respectively. Also shown are two possible  $\mu^+$  sites bound to tetra- and octahedral oxygen ions.

$\text{CaCO}_3$ . The data were corrected for a shape dependent macroscopic demagnetization field according to the procedure described in Ref. [6]. The magnitude of the Knight shift is small, on the order of 30 ppm, and negative. The negative sign of the shift can be explained by the spin polarization at the muon site. Although it was not possible to determine an exact muon location in the lattice, the small value of the Knight shift is consistent with the majority of previous measurements on metal oxide compounds, where the  $\mu^+$  is typically found bound to a single oxygen ion by creating a muoxyl bond  $(\text{O}\mu^+)^-$ . [5]

It has been established [1,2] that the majority of carriers in  $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$  are localized at molybdenum sites. Therefore, because of the effective screening of Mo ions by oxygen ions, one can anticipate a relatively low electronic spin density from those carriers on the  $\mu^+$ . This in turn leads to a value of  $\omega_\mu$  that is close to  $\omega_L$ . Also, it implies that, unlike in previously reported  $\mu\text{SR}$  results on  $s = 1/2$  AFM chain compounds [6], the muon charge does not act as a strong perturbation for the conducting chain. At the same time no significant change has been observed in the muon Knight shift around 25 K.

In order to further investigate a possible magnetic origin of the transition at 25 K, we performed a  $\mu\text{SR}$  experiment in a zero applied magnetic field (ZF). Figure 2 shows the results of this experiment. As seen, there are only slow  $1/T_1$  spin dynamics between RT and 4 K. The measured relaxation rate is rather small ( $\sim 0.2 \mu\text{s}^{-1}$ ), which is characteristic of a fast fluctu-

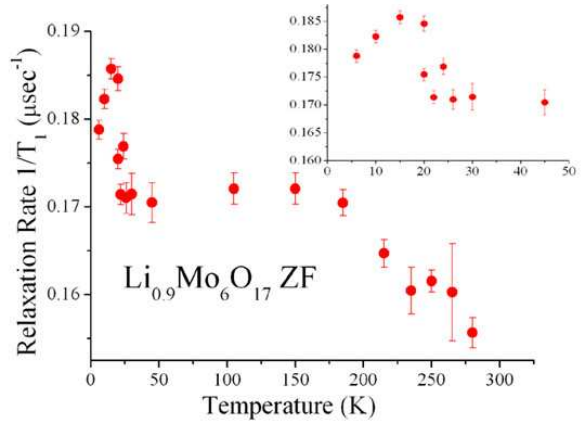


Fig. 2. Measured  $T$ -dependence of the muon spin relaxation rate. The inset shows the low temperature part around 25 K.

ating paramagnetic environment. The small downturn above 200 K can be attributed to motional narrowing due to rapid  $\mu^+$  diffusion at elevated temperatures.

At the same time, the small change ( $\sim 10\%$ ) in the  $\mu\text{SR}$  relaxation rate in the vicinity of  $T_x = 25$  K indicates that if a change in the ground state occurs around 25 K, it most probably is attributable to *increasing disorder* in the electronic environment to which the muon is coupled only indirectly via the change in a local environment.

This interpretation is consistent with the most recently reported optical studies where the role of disorder in the metal-insulator transition around 25 K it has been stressed [1]. Moreover, absence of any periodic modulation in the measured ZF spectra means that *no SDW is detected* in the sample. Thus the CDW ground state can be excluded. On the other hand, though less likely, one cannot exclude the possibility of very fast ( $\geq 10^9 \text{ s}^{-1}$ ) spin dynamics, which would be too fast to be observed on a  $\mu\text{SR}$  timescale.

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